Bioremediation of Contaminated Soils - Aquifers on Reilly Site in St. Louis Park

Status Report
June 15, 1992

Table of Contents

Section 1

Introduction

A. Objectives

The purpose of this study of the Reilly Superfund site is to investigate insitu remediation strategies for removing polynuclear aromatic hydrocarbons (PAH) which are major constituents of creosote impacted subsurface environments. Because this is a very common problem, the study has stressed development of innovative protocols that may have applications at other sites.

The rationale of the program reflects the findings that creosote associated organic chemicals are ultimately biodegradable, although rates of solubilization and biodegradation are known to depend on molecular weight-structure of the individual compounds. The program was designed to answer questions regarding:

- spatial distribution and composition of organic chemicals in the subsurface.
- water mobility of the major chemicals
- limitations on insitu biodegradations due to oxygen and nutrients
- permeability of the soils and its relation to insitu biodegradation
- development of mathematical models for design of bioremediation strategies.

This status report describes some of the new protocols that have been developed to obtain data to answer these questions. It also presents illustrative test data that have been obtained on soils and column tests. The first section describes procedures for sampling and analysis of subsurface soils. Procurement and setting up of minimally disturbed vertical profile soil cores for continuous flow testing are described in some detail because this protocol is capable of measuring fates of organics under conditions that approximate the field site. The third section presents data on rates of elution of PAH'S and related organics under no-growth conditions and with concurrent insitu biodegradation. Discussions of the mathematical modeling effort will be presented in a follow up report.

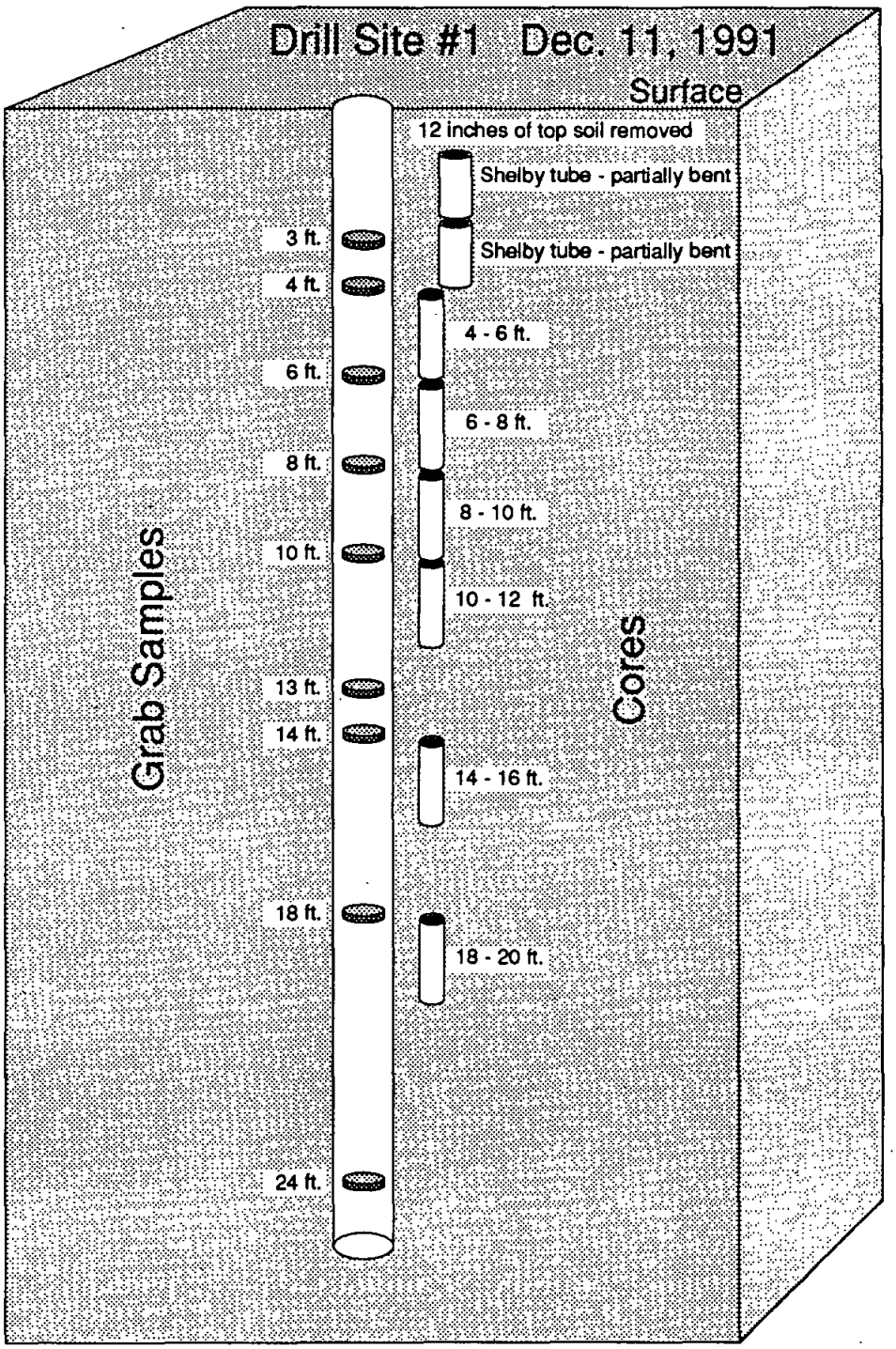
B. Sampling

The study has focused on the area referred to as Mount Reilly which was created as a temporary storage site for contaminated soils and was covered with top soil pending decisions regarding ultimate disposal. Because of the nonhomogenous nature of the site a series of borings were carried out to obtain soil samples for testing.

Figure 1.1 illustrates the sample gathering protocol for Drilling Site #1 which is one of three borings carried out December 11, 1991. A seven inch flight augur was used to initiate drilling. Minimally disturbed soil cores were taken in the form of two feet long, 2.5 inch diameter, stainless steel, split spoon inserts at the depths indicated. In addition, grab samples of soil were taken at the locations indicated when the bore hole was widened between split spoon sampling takes.

Two Shelby tube samples were taken near the surface. But use of Shelby tubes was discontinued because the tubes were too severely damaged. Depth locations of the split spoon core samples and the grab samples are identified in Figure 1.1. It can be seen that the split spoon sampling cores can be used to obtain an essentially complete vertical soil profile for laboratory testing. Test results on the grab samples and cores are presented in subsequent sections.

Figure 1.1 Sampling Protocol on 12/11/91 for Site #1 of the St. Louis Park Reilly Site



Section 2

Analysis of Polynuclear Aromatic Hydrocarbons (PAH's) in Soil Samples Obtained from the Reilly Site, St. Louis Park, MN.

A. Chemicals of Concern (COC)

PAH's listed below have been identified as the chemicals of concern based on previous surveys of the Reilly Site reported by MPCA , and the analytical protocols are designed to measure these PAH's:

Naphthalene	Phenanthrene	Benzo(a)anthracene	Benzo(a)pyrene
Acenaphthylene	Anthracene	Chrysene	Indeno(1,2,3-cd)pyrene
Acenaphthene	Fluoranthene	Benzo(b)fluoranthene	Dibenzo(a,h)anthracene
Fluorene	Pyrene	Benzo(k)fluoranthene	Benzo(g,h,i)perylene

Typical composition data for creosote (Table 2.1) shows that the predominant PAH's include some 17 compounds ranging from naphthalene with a solubility of 31.7 mg/L to Benzo(a)pyrene with a solubility of 0.003 mg/L. Phenolic and heterocyclic compounds are also present in creosote. However, the predominant phenols are very soluble as are most of the predominant heterocyclics. It is therefore likely that many of these chemicals will have been solubilized and transported off site. Nevertheless, a study is underway to estimate the total mass of organic chemicals that are present. More specifically, the total organic content as measured by combustion is being compared with the identified PAH concentrations to estimate unidentified mass of organic chemicals. The results will be reported in subsequent reports.

B. Soil Samples

The following soil samples were collected from the Reilly site in 250-ml glass bottles with gas-tight aluminum-lined lids, and were transported to the laboratory in coolers and stored in a 4°C cold room immediately upon arrival.

Sampling Date	Site#	Sampling Depths, ft.
10/9/91	1	4, 8, 13, 18, 24, 29
	2	2, 9, 14, 18
12/11/91	1	3, 4, 6, 8, 10, 13, 14, 18, 24

C. Soxhlet Extraction Procedures

The Soxhlet Extraction procedures described under EPA method 3540 was followed. The method is for extraction of nonvolatile and semivolatile organic compounds from solids, sludges, and wastes, and is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

1. Apparatus and Materials

   a. Soxhlet extractor:
   40-mm I.D., with 500-ml round-bottom flask.

   b. Kuderna-Danish (K-D) apparatus:
   Concentrator tube, 10-ml, graduated, Kontes.
   Evaporation flask, 500-ml, Kontes.
   Snyder column, 3-ball macro, Ace Glass,Inc.

   c. Boiling chips:
   PTFE boiling stones, solvent extracted, Norton co.

   d. Extraction thimbles:
   Cellulose extraction thimbles, single thickness, Whatman.

   e. Heating mantle:
   3-sample model, individually rheostat controlled, Fisher Scientific Co.

   f. Reagent water:
   Corning Mega-Pure water purification system.

   g. Sodium sulfate:
   Granular anhydrous, purified by washing with methylene chloride followed by heating at 400°C for 4 hours.

   h. Methylene chloride:
   OPTIMA grade, Fisher Scientific Co.

   i. 2-Fluorobiphenyl:
   Surrogate, 1000 mg/ml in methanol.

   j. Glassware:
   All laboratory glassware was cleaned according to the following procedures:
      a. Laboratory grade detergent wash and rinse.
      b. Multiple deionized water rinses.
      c. Acetone rinse.
      d. Oven dried (105°C) overnight.

2. Sample Preparation

   a. Foreign objects such as sticks, leaves, and gravels were discarded from the soil sample.

b. Ten (10) grams of soil sample were blended with 20 grams of anhydrous sodium sulfate until a dry homogeneous mixture was obtained.

c. The mixture was transferred to an extraction thimble, and 100 µg of 2-Fluorobiphenyl was added to the soil by transferring 100 µL of the surrogate stock solution using a syringe.

d. When moisture content of the soil sample was required, 10 grams of soil sample was weighed into a tared crucible and dried overnight at 105°C. The dried sample was weighed again after being cooled in a dessicator:

$$\% \text{ moisture} = \frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100$$

3. Extraction

a. Five hundred (500) ml of methylene chloride was added to the 500-ml round bottom flask containing one or two boiling chips.

b. The flask was attached to the extractor and extracted for 16-24 hours.

c. After the extraction was cooled and the extract cooled, the extract was concentrated to 10-ml using the K-D concentrator and the 3-ball Snyder column. The water temperature for concentration was adjusted (about 70°C) such that the concentration procedure was completed in approximately 30 minutes.

d. The concentrated extract was then analyzed for PAH's in the gas chromatograph.

4. Gas Chromatograph Analysis

EPA method 8000 (General Gas Chromatography) and EPA method 8100 (GC Analysis of Polynuclear Aromatic Hydrogen) were followed.

a. External Standard Calibration:

For each PAH of interest, calibration standards at a minimum of five concentration levels were prepared. One of the external standards was at a concentration near, but above, the method detection limit. The other concentrations corresponded to the expected range of concentrations found in real samples. Retention times were recorded for the identification of the analytes. Peak area responses were tabulated against the mass injected, and a calibration curve for each analyte was prepared. A second-order curve fitting equation was obtained for each analyte.

b. GC Analysis:

Conditions for GC analysis were as follows:

GC:	Hewlett Packard 5890 Gas Chromatograph with auto-sampler
Integrator:	Hewlett Packard 3396A Integrator
Column:	Hewlett Packard HP-5, 25m x 0.2mm x 0.33µm
Detector:	FID
Carrier gas:	hydrogen, 2ml/min
Initial T°:	40°C
Initial time:	1 min
Rate:	5°C/min
Final T°:	300°C
Final time:	10 min
Injection vol:	2 µL

D. Results

Results of PAH analysis of soil samples obtained from the St. Louis Park Reilly site on 10/9/91 and 12/11/91 are shown in Table 2.2. Sixteen PAH's have been identified in measurable quantities in most of the samples. Total concentrations are listed in the last column. All the profiles show vertical variations in concentrations. The following discussion of these variations focuses on the Site #1 samples of 12/11/91.

Figure 2.1 presents a histogram of the concentration profile. There are considerable variation in concentrations as a function of depth. The pattern is almost bimodal with high levels at depths 4-6 feet and in the vicinity of 14 feet. It has been suggested that the variations are due to concentration differences of the original deposited materials that were obtained from different parts of the site.

It is interesting to note that the "% of Total" for each compound is relatively constant as a function of depth as shown in Table 2.3. This suggests that the chemical mixtures are from similar sources. Naphthalene shows the largest variations in the upper soil horizons. This may be the result of vapor losses and/or the more rapid rate of biodegradation of this compound. The bar graph in Figure 2.2 shows the same data to highlight the variations in naphthalene as opposed to the almost constant "% of Total" values for phenanthrene and Benzo(a)pyrene as a function of soil depth.

E. Conclusions

The following conclusions can be drawn:

1. The sampling and analytical protocols give quantitative descriptions of the concentration distributions of the major PAH compounds. This information is essential for guiding bioremediation tests and for assessing oxygen and nutrient requirements.

2. The similarity in the vertical percentage distribution of all compounds indicates that the source materials were similar. This information is useful because it gives support to the idea that the kinetics of dissolution and biodegradation will be similar throughout the site.

Table 2.1 Principle Components in Coal Tar Creosote

Predominant polycyclic aromatic hydrocarbons in coal tar creosote

Compound	Relative percentage (wt)	MW	Aqueous solubility (mg/L,25°C)
Naphthalene	13	128.2	31.7
2-Methylnaphthalene	13	142.2	25.4
Phenanthrene	13	178.2	1.3
Anthracene	13	178.2	0.07
1-Methylnaphthalene	8	142.2	28.5
Biphenyl	8	154.2	7.5
Fluorene	8	166.2	2.0
2,3-Dimethylnaphthalene	4	156.2	3.0
2,6-Dimethylnaphthalene	4	156.2	2.0
Acenaphthene	4	154.2	3.9
Fluoranthene	4	202.3	0.26
Chrysene	2	228.2	0.002
Pyrene	2	202.3	0.14
Anthraquinone	1	208.2	-
2-Methylanthracene	1	192.3	0.04
2,3-Benzo(b)fluorene	1	216.3	0.002
Benzo(a)pyrene	1	252.3	0.003

Predominant phenolic compounds in coal tar creosote

Compound	Relative percentage (wt)	MW	Aqueous solubility (mg/L,)
Phenol	20	94.1	82,000 (15°C)
0-Cresol	10	108.1	25,920 (25°C)
m-Cresol	10	108.1	23,500 (25°C)
p-Cresol	10	108.1	24,000 (40°C)
Pentachlorophenol	10	266.4	14 (20°C)
2,5-Xylenol	7.5	122.2	3,544 (25°C)
3,5-Xylenol	7.5	122.2	4,888 (25°C)
2,3-Xylenol	5	122.2	4,570 (25°C)
2,4-Xylenol	5	122.2	6,232 (25°C)
2,6-Xylenol	5	122.2	6,049 (25°C)
3,4-Xylenol	5	122.2	4,766 (25°C)
2,3,5-Trimethylphenol	5	136.3	-

Predominant heterocyclic compounds in coal tar creosote

Compound	Relative percentage (wt)	MW	Aqueous solubility (mg/L,)
N-Heterocyclics and N-containing aromatics			
Quinoline	10	129.2	6,718 (20°C)
Isoquinoline	10	129.2	4,522 (20°C)
Carbazole	10	167.2	1 (20°C)
2,4-Dimethylpyridine	10	107.2	-
Acridine	5	179.2	5 (20°C)
Aniline	5	93.1	3,400 (25°C)
2-Methylquinoline	5	143.2	-
4-Methylquinoline	5	143.2	-
Pyrrole	5	67.1	-
Pyrrolidine	5	71.2	-
S-Heterocyclics			
Benzo(b)thiophene	10	134.2	130 (20°C)
Dibenzothiophene	10	184.3	2 (24°C)
O-Heterocyclics			
Dibenzofuran	10	168.2	10 (25°C)

Table 2.2 PAH Analysis of Soil Samples Obtained from the St. Louis Park Reilly Site on 10/9/91 and 12/11/91

Sampling Date	Site No.	Depth (ft)	PAH Concentration, mg per Kg Soil															
			NAPH	ACNY	ACNE	FLUO	PHEN	ANTH	FLAN	PYRN	BAAN	CHRY	BBFN	BKFN	BAPY	INPY	DBAN	BPER	Total
10/9/91	1	4	40.12	7.17	22.23	32.57	75.54	59.81	51.06	37.89	19.24	22.78	15.94	8.95	16.37	24.38	19.86	19.60	473.51
		8	92.04	6.16	75.77	69.74	163.97	54.09	126.16	89.23	29.65	33.97	19.93	15.49	18.23	20.78	16.76	17.03	849.00
		13	42.21	10.32	31.58	33.18	91.08	31.88	107.88	86.66	33.41	45.52	30.87	21.94	28.36	29.05	20.30	25.39	669.63
		18	36.88	6.64	33.15	33.34	78.04	33.11	75.50	58.37	24.21	30.01	20.15	17.89	19.42	23.94	19.69	20.06	530.40
		24	6.33	1.29	8.64	8.80	25.25	9.89	22.23	16.72	5.94	7.88	5.05	2.80	4.59	4.58	3.09	4.16	137.24
		29	10.09	1.42	11.00	10.95	31.21	12.19	26.29	19.52	6.54	8.50	5.51	2.86	5.00	4.88	3.12	4.22	163.30
	2	2	1.47	1.38	0.87	1.89	4.78	3.70	6.34	5.80	3.65	5.59	5.24	2.57	4.05	6.23	3.34	7.04	63.94
		9	0.24	0.13	0.28	0.48	1.59	1.29	1.45	1.55	0.58	1.06	0.62	0.52	0.43	0.57	0.35	0.51	11.65
		14	0.35	0.22	0.79	0.75	2.59	2.65	4.88	4.00	1.57	2.43	1.59	1.21	1.29	1.12	0.51	1.01	26.96
		18	0.24	0.15	0.29	0.27	0.61	0.48	1.29	1.09	0.54	0.98	0.71	0.39	0.52	0.65	0.39	0.67	9.27
12/11/91	1	3	6.43	3.98	9.38	19.42	58.28	32.10	49.25	39.61	19.23	25.42	19.92	13.41	17.55	13.61	0.52	13.21	341.32
		4	16.99	5.02	40.59	47.91	195.11	71.86	203.99	155.76	72.15	89.31	69.68	64.66	61.02	36.51	10.32	36.07	1176.95
		6	80.63	2.99	75.15	74.83	195.49	116.51	131.24	94.97	38.96	51.49	34.82	ND	27.02	19.01	ND	18.80	961.91
		8	61.14	2.64	62.92	54.84	135.16	60.49	133.82	99.83	44.59	63.19	45.26	21.69	34.46	22.19	ND	21.72	863.94
		10	25.11	1.59	33.07	31.84	86.31	70.80	81.52	67.18	27.89	43.79	28.44	ND	21.83	13.42	1.45	15.10	549.34
		13	62.51	10.10	49.17	47.83	148.94	60.89	161.77	136.26	69.34	112.49	74.96	64.08	63.78	37.69	13.61	36.77	1150.19
		14	70.08	14.46	68.98	70.33	241.15	86.64	244.97	207.87	97.90	169.26	100.37	75.80	85.43	51.27	21.22	46.94	1652.67
		18	58.08	6.61	50.19	46.02	153.06	72.60	158.47	132.49	59.80	88.91	57.52	51.91	48.94	30.48	9.20	28.58	1052.86
		24	29.17	4.41	35.63	35.53	115.07	51.44	116.93	93.95	44.82	66.50	39.21	36.88	33.39	21.01	5.03	18.50	747.47

Legends

NAPH	Naphthylene	BAAN	Benzo(a)anthracene	ND	Non-detectable
ACNY	Acenathylene	CHRY	Chrysene		
ACNE	Acenaphthene	BBFN	Benzo(b)fluoranthene		
FLUO	Fluorene	BKFN	Benzo(k)fluoranthene		
PHEN	Phenanthrene	BAPY	Benzo(a)pyrene		
ANTH	Anthracene	INPY	Indeno(1,2,3-cd)pyrene		
FLAN	Fluoranthene	DBAN	Dibenzo(a,h)anthracene		
PYRN	Pyrene	BPER	Benzo(g,h,i)perylene		

Table 2.3 Percentage Distribution of Total PAH's in Soil Samples from Site 1 of the St. Louis Park Reilly Site

Sampling Date	Site No.	Depth (ft)	% of Total PAH's														
			NAPH	ACNY	ACNE	FLUO	PHEN	ANTH	FLAN	PYRN	BAAN	CHRY	BBFN	BKFN	BAPY	INPY	DBAN	BPER
12/11/91	1	3	1.88	1.17	2.75	5.69	17.07	9.40	14.43	11.60	5.63	7.45	5.84	3.93	5.14	3.99	0.15	3.87
		4	1.44	0.43	3.45	4.07	16.58	6.11	17.33	13.23	6.13	7.59	5.92	5.49	5.18	3.10	0.88	3.06
		6	8.38	0.31	7.81	7.78	20.32	12.11	13.64	9.87	4.05	5.35	3.62	0.00	2.81	1.98	0.00	1.95
		8	7.08	0.31	7.28	6.35	15.64	7.00	15.49	11.56	5.16	7.31	5.24	2.51	3.99	2.57	0.00	2.51
		10	4.57	0.29	6.02	5.80	15.71	12.89	14.84	12.23	5.08	7.97	5.18	0.00	3.97	2.44	0.26	2.75
		13	5.43	0.88	4.27	4.16	12.95	5.29	14.06	11.85	6.03	9.78	6.52	5.57	5.55	3.28	1.18	3.20
		14	4.24	0.87	4.17	4.26	14.59	5.24	14.82	12.58	5.92	10.24	6.07	4.59	5.17	3.10	1.28	2.84
		18	5.52	0.63	4.77	4.37	14.54	6.90	15.05	12.58	5.68	8.44	5.46	4.93	4.65	2.89	0.87	2.71
		24	3.90	0.59	4.77	4.75	15.39	6.88	15.64	12.57	6.00	8.90	5.25	4.93	4.47	2.81	0.67	2.48

Legends

NAPH	Naphthylene	BAAN	Benzo(a)anthracene
ACNY	Acenathylene	CHRY	Chrysene
ACNE	Acenaphthene	BBFN	Benzo(b)fluoranthene
FLUO	Fluorene	BKFN	Benzo(k)fluoranthene
PHEN	Phenanthrene	BAPY	Benzo(a)pyrene
ANTH	Anthracene	INPY	Indeno(1,2,3-cd)pyrene
FLAN	Fluoranthene	DBAN	Dibenzo(a,h)anthracene
PYRN	Pyrene	BPER	Benzo(g,h,i)perylene

Figure 2.1 PAH Concentrations in Soil Samples from Site #1 of the St. Louis Park Reilly Site (sampled on 12/11/91)

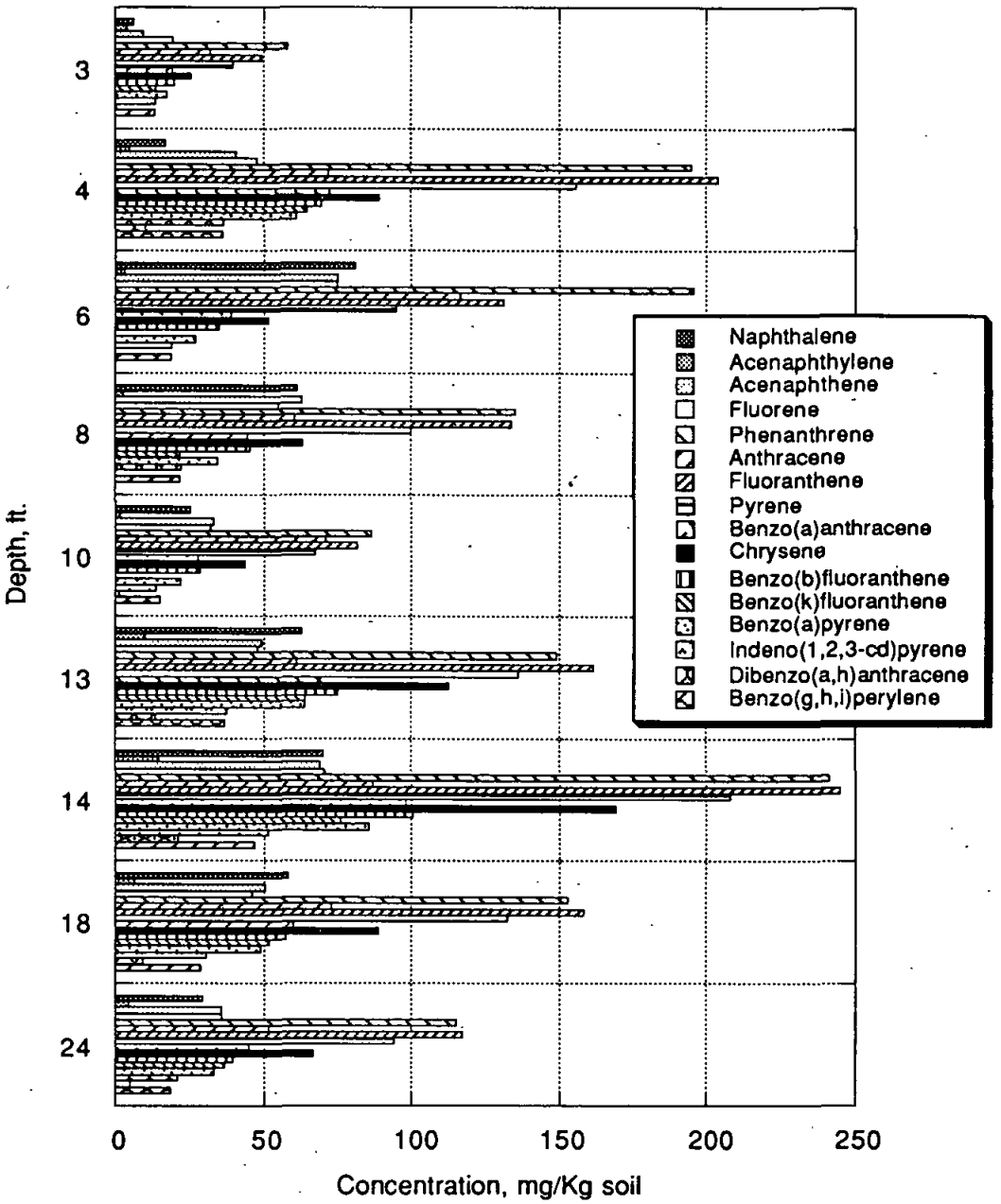
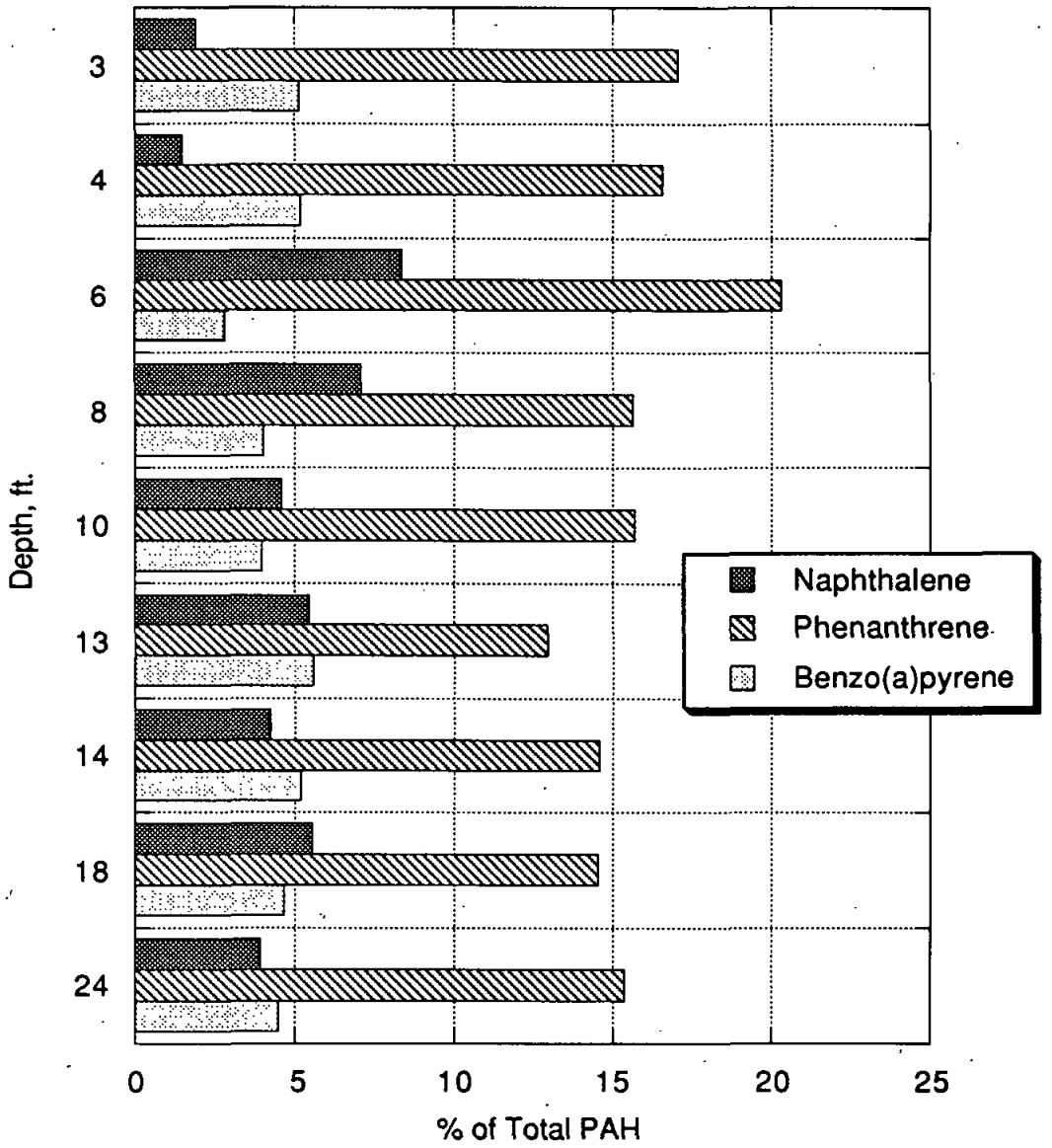


Figure 2.2 Distribution of Total PAH's for Naphthalene, Phenanthrene, and Benzo(a)pyrene in Soil Samples from Site #1 of the St. Louis Park Reilly Site (sampled on 12/11/91)



Section 3

Split Spoon Insert Column Studies
Column Setup and Analytical Protocol

A. Apparatus for testing Minimally Disturbed Aquifer Materials Split Spoon Insert Columns (SSIC)

Development of protocols for obtaining minimally disturbed samples of contaminated soils for testing in the laboratory was a critical initial objective of this research program. Testing of minimally disturbed soils is deemed essential for defining rate data needed to assess the feasibility of insitu cleanup of contaminated aquifers. For this reason, a program for taking cores of aquifer materials by drilling with split spoon samplers with stainless steel inserts and adapting the filled tubes for column studies was undertaken. Needless to say, the procedures could have application at other sites. Construction and operating procedures of Split Spoon Insert Columns (SSIC) are described below.

1. Split Spoon Insert Column Description

The column is the insert from a split spoon sampler containing an undisturbed soil core. As shown in Figure 3.1, the column is 24 inches long with an id of 2 3/8 inches and an O.D. of 2 1/2 inches. The ends of the column are sealed at either end with an aluminum cap. The caps are square blocks of aluminum, 4.5 inches per side with a thickness of 1/2 inch. A circular groove the same diameter as the column and 0.125 inches wide was cut into the center of aluminum block. A rubber o-ring was inserted in this groove to seal the column to the cap. Three bolts running from the bottom base plate to the top plate secure the base plates to the column. The center of the cap was drilled and tapped to fit an 1/8 inch stainless steel swagelock fitting.

The column is equipped with 7 sampling ports located at 3 inch intervals on alternating sides of the column. The ports are constructed from 1/2 inch diameter stainless steel sleeves inserted into holes drilled into the side of the column. The sleeves are sealed to the column with a silicon epoxy. A mini-inert valve is inserted into each sleeve. The valve, as shown in Figure 3.2, is of all Teflon construction and is equipped with a rubber septa which allows insertion of a needle to withdraw water samples from the soil core while maintaining an airtight seal. The mininert valves can be removed to allow removal of soil samples.

The water is fed to the column through 1/8 inch stainless steel tubing. The tubing is connected to the column with 1/8 inch swagelock stainless steel fittings. The water is pumped through the column using a Gilson Minipuls 2, 4-channel pump. Each column is assigned to one of the four channels The pump is set up with a 1.52 mm I. D. pump tube with a flow rate of 0.3 ml/min.

2. Core Descriptions

At the present time three soil cores are being tested, and are numbered sequentially one to three from the date testing started. The cores were obtained from different depths at the same site located on the ridge running along the western edge of the Reilly site:

Number	Date Started	Depth
1	3/1/92	6'-8'
2	6/3/92	10'-12'
3	6/5/92	4'-6'

The soil in the columns contains a mix of layers of different soil types including silty sand, medium sand, peat and clay. The water content of the soil was approximately 10% by weight. The porosity of the soils was 30 % and the average solids density was 2.64 g/cm^3. The chemical properties of the soil is being tested but the data is unavailable at this time.

B. Column Preparation

The drilling to obtain the split spoon insert cores was done on December 11, 1991. The full split spoon inserts were weighed and the ends sealed with plastic caps in the field. The inserts were stored in a temperature controlled room at 10°C until needed. Before testing the split spoon insert was opened and approximately 50 grams of soil was remove from both the top and bottom of the core. This soil was tested to find the physical and chemical characteristics of the soil. A Soxhlet extraction was performed on a 10 g sample of the removed soil to find the concentration of the targeted contaminants in the soil.

After the soil samples are removed the top and bottom of the insert is sealed with a Styrofoam pug and resealed with the plastic cap. The insert was taken to the Civil and Mineral Engineering machine shop. The personnel at the machine shop installed the seven sampling ports and returned the insert to the lab. In the lab the Styrofoam was removed from both ends of the insert. The space between the soil core and the end of the column was filled with washed and sieved Jordan aquifer sand. Two screens were placed on the top of the sand. The first screen is a fine mesh designed to allow water to enter and exit but retain the soil particles. The second screen is a course mesh with drainage channels cut into the center. It is designed to direct the water flow to the outflow fitting of the column. The insert is capped on both ends and installed onto a stand.

The water supplied to the column was deoxygenated to an oxygen content of 0.1-0.5 mg/l by sparging nitrogen into a 5 gallon carboy of de ionized water. To begin the flow of water through the column the inlet and outlet tubes are connected to the column to provide up flow. The reverse flow was used to ensure that the soil core was completely saturated. The pump flow rate was set to 0.3 ml/min. and the column was filled until water began to flow from the outlet. Once the flow from the top of the column was established the inlet and outlet tubes were reversed so that the remainder of the experiment was performed with down flow.

C. Sampling Procedures-Anoxic Conditions

1. Glassware

All of the glassware was cleaned using the following procedure:
a. Soap wash
b. Rinsed and soaked in de-ionized water
c. Air dried
d. Rinsed in acetone
e. Oven dried at 105°C for 24 hours

2. Effluent Sampling

The water run through the column is anoxic to prevent biological activity in the column. The oxygen concentration in the water is sufficient to allow free bacteria in the effluent some biodegradation. To inhibit this bacterial growth in the effluent sample the sample is collected in 500 ml Erlenmeyer flasks which have approximately 0.75g of Sodium Azide added and are purged with nitrogen prior to being used.

The effluent sample is collected over a 24 hour period yielding a total sample volume of 400 to 435 milliliters depending on the average flow rate of the sampling period.

D. Effluent Analysis

1. Dissolved Oxygen and pH Measurements

The effluent is tested for dissolve oxygen concentration immediately after the flask is removed from the column. The oxygen level is determined with an Orion oxygen electrode connected to an Orion SA 520 pH meter. The pH of the sample is taken with the same meter.

2. Solid Phase Extraction

A 10 ml aliquot of the sample is removed from the flask with a 10 ml gas tight syringe and injected into a 10 ml screw cap test tube. Five µl of a surrogate spike, 2-Fluorobiphenyl 5000 mg/l in methanol, is injected into the 10 ml aliquot. The spike is added to track the efficiency of the solid phase extraction of the samples. The non-polar organic in the aliquot are extracted and concentrated via a solid phase extraction technique.

a. Equipment:

Varian 500 mg Bond Elut Octadecyl (C-18) cartridges
Varian Vac Elut vacuum source
2 ml class A volumetric test tubes.

Fisher Optima grade hexane
Fisher Optima grade methanol

b. Procedure:

The procedure used is given by Varian for general non-polar isolates. The cartridge is inserted into the vacuum source. One to two ml of methanol is passed through the cartridge to activate the sorbent. The cartridge is immediately rinsed with 1 to 2 ml of de-ionized water. Immediately after the rinsé water has passed the sample is applied to the cartridge. After the sample has passed through the cartridge the cartridge is removed from the vacuum source and allowed to dry over night.

The non-polar isolates are extracted from the C-18 sorbent by passing a 2-ml aliquot of hexane through the cartridge and collecting it in a 2-ml volumetric test tube. The hexane which is lost due to volatilization during the extraction process is replaced so that the test tube is filled to the 2-ml mark. The final extract is a five-fold concentration of the original sample aliquot.

3. Gas Chromatographic Analysis

EPA method 8000 (General Gas Chromatography) and EPA method 8100 (GC Analysis of Polynuclear Aromatic Hydrocarbons) were followed.

a. External Standard Calibration:

For each PAH of interest, calibration standards were made using 99.9% pure compounds dissolved in Optima grade hexane. A minimum of five concentration levels were prepared. The concentration levels began near but not below the detection limit of the instrument, the rest of the standards at levels expected of the real samples. The peak areas were compared against the mass injected and a calibration curve was developed for each analyte. A second order polynomial fit was prepared for each analyte.

b. GC Analysis Parameters:

Two injections from each sample extract was performed on the GC under the following conditions:

GC	Hewlett Packard 5890 with auto sampler
Integrator	HP 3396
Column	HP-5, 25m x 0.2 mm x .33µm
Detector	FID
Carrier Gas	Hydrogen, 2ml/min
Initial Temp	40°C
Initial Time	1 min.
Rate	6°C/min
Final Temp	260°C
Final Time	10 min
Injection vol	2 µl

E. Intermediate Column Samples

Intermediate samples were taken along the length of the column through the sampling ports. These sample were taken about every other week.

1. Port Sampling Method

To sample the ports a 10-ml syringe, with the plunger removed and a 4-inch, 22 gauge needle was used to penetrate the septum of the mininert valve in the sampling port. Once the septum was penetrated and a flow into the syringes was established the syringe was clamped to a stand and allowed to fill. The syringe filled by the flow from the port alone the plunger was not used to draw out a sample. This was done to prevent desaturating the column and to provide a more representative sample of the column water at the position of the port.

The ports were sampled sequentially from the top of the column to the bottom. Each sample takes about 20-30 minutes to collect.

2. Analysis

The samples from the ports were extracted and analyzed using the same methods as the effluent samples, except that pH and dissolved oxygen content were not measured.

Figure 3.1 Schematic of a 2.5-Inch Diameter Stainless Steel Column

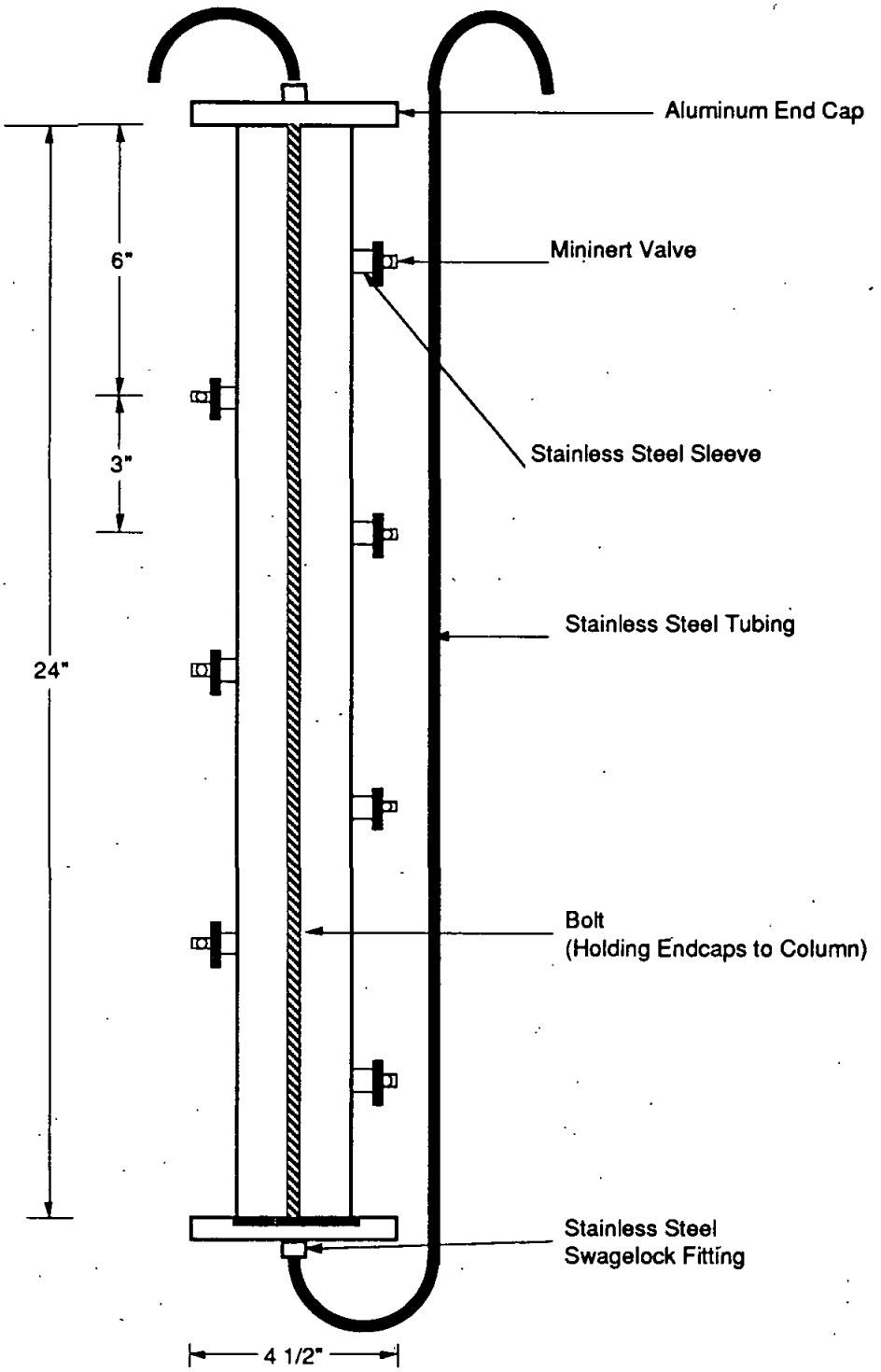
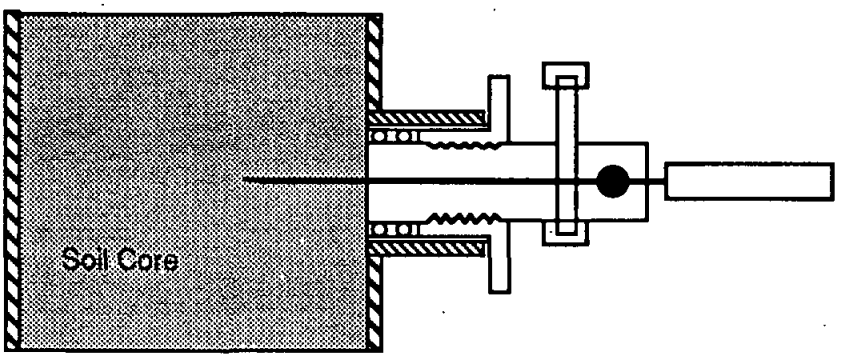


Figure 3.2 Cut-Away View of a Mininert Valve

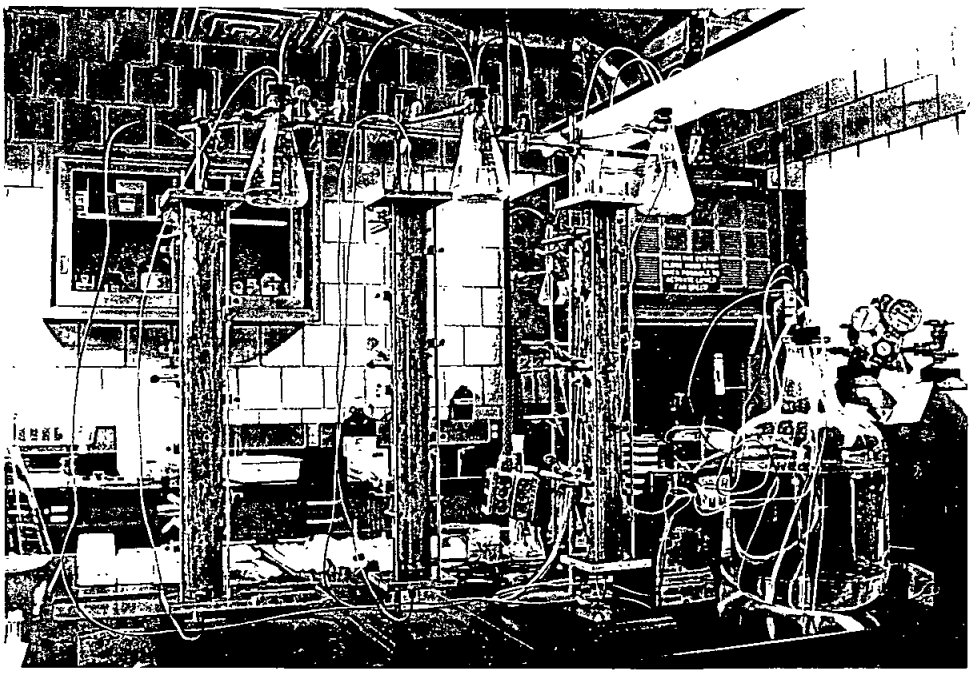


Section 4

Split Spoon Insert Column Studies
Results and Conclusions

A. General Operations of the Split Spoon Insert Columns (SSIC)

Three split spoon insert column soil cores from the Reilly site are currently being tested to measure rates of removal of creosote related organic chemicals. The apparatus is shown in the photograph below.



Descriptions of the core materials, column preparation, and operating conditions are described in the previous section. More detailed descriptions of the procurement (drilling and site descriptions) of the SSIC cores have been presented in an earlier report.

Column #1 has been in operation for over 3,000 hours with continuous dosing. Columns #2 and #3 have been in operation for over 700 hours. During this period, samples of water from the outlet and at intermediate sampling port have been taken periodically and analyzed using an adaptation of EPA prescribed analytical procedures for concentrating and measuring PAH's by GC analysis as described in the previous section.

Prior to initiating the tests, composited samples of soil taken from the inlet and outlet of each column were analyzed. Concentrations from column test #1 are shown in Table 4.1.

The chemical composition of the composite is consistent with the composition of the grab samples for the same depth of soil shown in Table 2.2. Concentrations are expressed in terms of mg-compound /Kg soil. Fifteen compounds were identified, ranging from naphthalene to Benzo(g,h,i)perylene which represent progressively higher molecular weights and lower volatilities. It is noteworthy that the intermediate compounds show the highest concentration in line with the measurements of the grab samples described above. It is not known to what extent this reflects the effects of weathering and insitu biodegradation of the more volatile species as opposed to differences in initial distribution and composition of the creosote source materials. Additional testing will be carried out to try to resolve this question. Additional data will be coming from the other cores, and will be examined to see if they show the same trends. The data will then be analyzed using statistical methods to define spatial variability in order to describe concentration distribution ranges.

Conclusions:

1. Soxhlet analyses of the soil are used as indicators of the chemicals that are expected to be measured in the effluent water samples, keeping in mind that water solubilities are progressively lower with increasing molecular weight.

2. For future reference, consideration should be given to taking samples of soil at intermediate points to define initial concentration distribution more precisely albeit this will result in some disturbance of the hydraulic characteristics of the soil core.

B. Column #1

1. Initial Operations

Effluent concentrations of the eight PAH's that were detected consistently during the first 700 hours of dosing are shown in Table 4.2. The same data are shown graphically in Figures 4.1 - 4.8. The day to day variations in concentration were larger than expected and it was found that most of these variations were due to experimental problems that have since been eliminated. The causes of these problems and their solution are briefly summarized to show that the SSIC testing protocol is reliable but requires attention to operating procedures, particularly with regard to access to molecular oxygen and handling of samples prior to analysis.

One problem was caused by diffusion of oxygen from the air through the plastic tubing that was used to pump deoxygenated water to the column. It had been decided to initiate the test by using anoxic conditions to test removal of organics by flushing without biodegradation. As a result availability of oxygen and hence degree of removal of organics varied. Plastic tubing was replaced with stainless steel. The second problem resulted from biodegradation of organics in the collection vessel caused by the presence of microbial cells and oxygen. This problem was solved by adding sodium azide to the collected effluent to stop microbial activity. It should be noted that the observed biological removal of

organics is actually desirable from a practical viewpoint because it is evidence that microbial activity is capable of removing the target chemicals. However, for this first phase of the study, the objective was to measure the rates of elution with minimal biological activity. This type of information is needed to quantify the physical rates of removal, namely desorption and dissolution and subsequent transport of the solubilized species through the rest of the column.

2. Stabilized Operations

Effluent concentrations of the four most significant chemicals for the time period from 850 to 2700 hours are shown in Figures 4.9 - 4.12. They show much less scatter; furthermore, concentration levels are higher because biodegradation (insitu and in collection vessel) was essentially eliminated. Effluent concentrations show a consistent downtrend with time; the trend is most significant with naphthalene and least with the higher molecular weight compounds which elute at the lowest concentrations.

To put these numbers in perspective, the time integrated total mass of chemicals eluted over the first 3000 hours have been calculated and compared with the initial mass as measured by Soxhlet extraction at the beginning of the test (see Table 4.1). Percent removal as measured by effluent concentrations are up to 19% for naphthalene but progressively smaller for the other chemicals, namely 6.2% for acenaphthene, 3.4% for fluorene, and less than 1% for phenanthrene. It is important to note that phenanthrene removal is very small despite the fact that it is present at the highest concentration in the soil. The data for the higher molecular weight chemicals have not been calculate yet.

Conclusions:

1. Column tests generate a large data base which gives insight on relative rates of leaching of specific compounds.

2. Rates of leaching are slow but significant.

3. Overall mass balances on each chemical give qualitative insight on rates of leaching but will have to be checked by taking soil samples in the near future.

4. Data must be analyzed using transport models to quantify the partitioning relationships of each compound between the water phase and soil phases. This is essential for developing the necessary correlations as tools for engineering application studies.

3. Concentration Profiles at Intermediate Points

As indicated in the procedures section, water samples were taken from each of the intermediate sampling ports in order to measure concentration distributions at selected time intervals. Five concentration depth profiles from column #1 are shown in Figures 4.13 and 4.14. The depth measurement is given with reference to the top of the column. The soil bed starts at approximately 5.5

inches in part due to the fact that some soil was removed from the inlet and outlet of each column for testing as described previously.

Increases in concentration in the downstream direction were not unexpected because of the cumulative contact time between water and soil phases. However, the downward concentration trends in the lower half of the column are due to other causes. One possibility is that there was nonuniform distribution of chemicals in the bed initially. Another possibility is that continuous leaching of the column has resulted in a substantial concentration gradient in soil organic content (foc). This could result in readsorption of chemicals in those parts of the bed with the highest foc.

As of this writing, concentration profiles have also been obtained on each of columns #2 and 3 but the data are not yet available. It is expected that the qualitative explanation for the shape of the concentration profiles will become clearer once all the data are in. However, data analysis in terms of transport models is essential to obtain quantitative descriptions, e.g.. parameter estimation by fitting the concentration profiles.

Conclusion:

1. Concentration profiles (snapshots in time) show some expected as well as unexpected results.

2. Explanations will be sought by modeling/parameter estimation.

C. Sampling and Analysis of Soils from Intermediate Points in the Columns

We have so far refrained from taking soil samples from intermediate points in the column to avoid disturbing the structure of the soil core and its hydraulic characteristics. However, it would be advantageous from the standpoint of modeling the sequence of events in the column if the concentration distribution in the soil column could be established. To this end we have very recently initiated a series of pressure drop tests at sequential point in the columns and overall chloride breakthrough measurements in order to characterize flow distributions. These test will be repeated after soil samples have been taken as an indicator of the effects of removing small amounts of soil at intermediate locations in the beds.

Table 4.1 PAH Analysis of a Composite Soil Sample from the St. Louis Park Reilly Site

Date of Sampling:	11/25/92
Type of Sample:	Split Spoon Core
Site:	#1
Depth:	6 - 8 ft.
Total Weight of Sample:	2.42 Kg
Amount of Soil Extracted:	10 gm
Final Volume of Extract:	10 ml

Compound	mg/Kg Soil	Total Weight (mg)	Weight Removed (mg)	Percent Removed	Weight Remaining (mg)
Naphthalene	51.38	124.34	23.61	18.99	100.73
Acenaphthylene	4.60	11.13	N/A	N/A	N/A
Acenaphthene	79.69	192.85	11.97	6.21	180.88
Fluorene	75.46	182.61	6.28	3.44	176.33
Phenanthrene	198.61	480.64	4.66	0.97	475.98
Anthracene	97.10	234.98	N/A	N/A	N/A
Fluoranthene	153.69	371.93	N/A	N/A	N/A
Pyrene	121.03	292.89	N/A	N/A	N/A
Benzo(a)anthracene	40.46	97.91	N/A	N/A	N/A
Chrysene	56.94	137.79	N/A	N/A	N/A
Benzo(b)fluoranthene	33.44	80.92	N/A	N/A	N/A
Benzo(k)fluoranthene	29.94	72.45	N/A	N/A	N/A
Benzo(a)pyrene	25.62	62.00	N/A	N/A	N/A
Indeno(1,2,3-cd)pyrene	17.28	41.82	N/A	N/A	N/A
Dibenzo(a,h)anthracene	0.00	0.00	N/A	N/A	N/A
Benzo(g,h,i)perylene	17.00	41.14	N/A	N/A	N/A

Table 4.2 PAH Concentrations in Effluent from Column #1

	Time, hr	NAPH	ACNY	ACNE	FLUO	PHEN	ANTH	FLAN	PYRN
1	0.000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
2	16.580	0.005420	0.000670	0.061710	0.034250	0.017620	0.004660	0.002680	0.001620
3	26.250	0.061350	0.001610	0.118480	0.069090	0.058500	0.012520	0.008080	0.004740
4	37.750	0.363010	0.001780	0.141650	0.078250	0.066770	0.015750	0.010530	0.006100
5	48.250	0.239150	0.002630	0.145300	0.083100	0.082390	0.018870	0.013540	0.008160
6	60.920	0.501940	0.002440	0.152160	0.417750	0.086550	0.020150	0.015150	0.008970
7	73.940	0.402380	0.002410	0.141150	0.077780	0.081600	0.018660	0.074390	0.009160
8	87.440	0.527280	0.002420	0.150580	0.081030	0.084880	0.020550	0.018130	0.011080
9	95.940	0.500140	0.002500	0.140380	0.080040	0.076650	0.019900	0.017800	0.010990
10	107.670	0.623400	0.003580	0.159330	0.085440	0.090540	0.020980	0.021180	0.013350
11	117.670	0.516370	0.002570	0.147970	0.083150	0.088870	0.021570	0.020500	0.012810
12	131.170	0.539800	0.002830	0.151280	0.077520	0.075560	0.022180	0.018640	0.011650
13	142.020	0.520820	0.004090	0.148490	0.079400	0.080040	0.020370	0.019370	0.012410
14	154.730	0.599630	0.004010	0.147010	0.075480	0.074030	0.020120	0.018810	0.012350
15	166.430	0.271600	0.002740	0.130280	0.069970	0.070710	0.018230	0.018360	0.011330
16	176.480	0.307880	0.002930	0.146510	0.076770	0.078550	0.019290	0.019710	0.012330
17	184.540	0.428110	0.002810	0.150300	0.078880	0.086390	0.020070	0.018890	0.011680
18	197.920	0.251080	0.002850	0.151440	0.073040	0.070160	0.020640	0.022180	0.014200
19	207.040	0.352430	0.002650	0.138790	0.078240	0.086210	0.022000	0.024280	0.015390
20	220.560	0.468520	0.002810	0.141750	0.074850	0.072890	0.021450	0.020570	0.012540
21	233.560	0.584330	0.003050	0.170620	0.082420	0.082830	0.021420	0.023950	0.014850
22	245.690	0.573970	0.002620	0.157990	0.080220	0.084930	0.022630	0.024040	0.014940
23	254.360	0.411210	0.002990	0.137850	0.073710	0.078310	0.018808	0.019040	0.011150
24	268.270	0.433480	0.003090	0.156900	0.074500	0.072810	0.019720	0.022280	0.013670
25	278.350	0.479880	0.002430	0.136900	0.070590	0.072400	0.016610	0.020430	0.012610
26	293.710	0.422950	0.002970	0.155920	0.067300	0.043340	0.015250	0.022930	0.014710
27	305.560	0.503220	0.002530	0.140720	0.074410	0.068620	0.017340	0.021540	0.013310
28	329.640	0.000000	0.000000	0.000000	0.019010	0.000000	0.000000	0.016610	0.010720
29	341.307	0.005870	0.002710	0.146130	0.068170	0.037830	0.011980	0.020450	0.011940
30	368.307	0.004070	0.001450	0.089200	0.042380	0.015150	0.008290	0.014560	0.008770
31	391.307	0.415210	0.002100	0.123940	0.060820	0.063320	0.017500	0.017450	0.010970
32	415.557	0.414860	0.001580	0.119060	0.061800	0.060420	0.010600	0.013840	0.007630
33	439.557	0.000000	0.000870	0.097200	0.051730	0.029780	0.010720	0.012510	0.006650
34	458.167	0.464860	0.001700	0.125840	0.063810	0.062470	0.010580	0.013340	0.007260
35	485.167	0.473530	0.001800	0.129950	0.066680	0.066880	0.011810	0.014450	0.008130
36	512.320	0.462980	0.002220	0.130410	0.067530	0.070570	0.013140	0.017010	0.009970
37	537.320	0.676760	0.005390	0.191320	0.106960	0.118250	0.029890	0.029800	0.018290
38	559.120	0.399550	0.001720	0.130920	0.070420	0.075950	0.015520	0.017630	0.010510
39	583.140	0.288560	0.000990	0.090230	0.047960	0.047720	0.008120	0.010100	0.006380
40	607.200	0.266430	0.000880	0.082740	0.044220	0.044070	0.008590	0.008870	0.005050
41	631.500	0.272470	0.000990	0.089360	0.047370	0.047610	0.008030	0.010480	0.005970
42	654.500	0.354340	0.001420	0.120600	0.064700	0.071770	0.014650	0.018620	0.011060
43	679.600	0.416660		0.120990	0.102800	0.075150			
44	699.600	0.410510		0.126250	0.111480	0.082810			

Legends:

NAPH	Naphthalene	ACNY	Acenaphthylene
ACNE	Acenaphene	FLUO	Fluorene
PHEN	Phenanthrene	ANTH	Anthracene
FLAN	Fluoranthene	PYRN	Pyrene

Figure 4.1 Naphthalene Concentration in Effluent from Column #1 (0-700 hr)

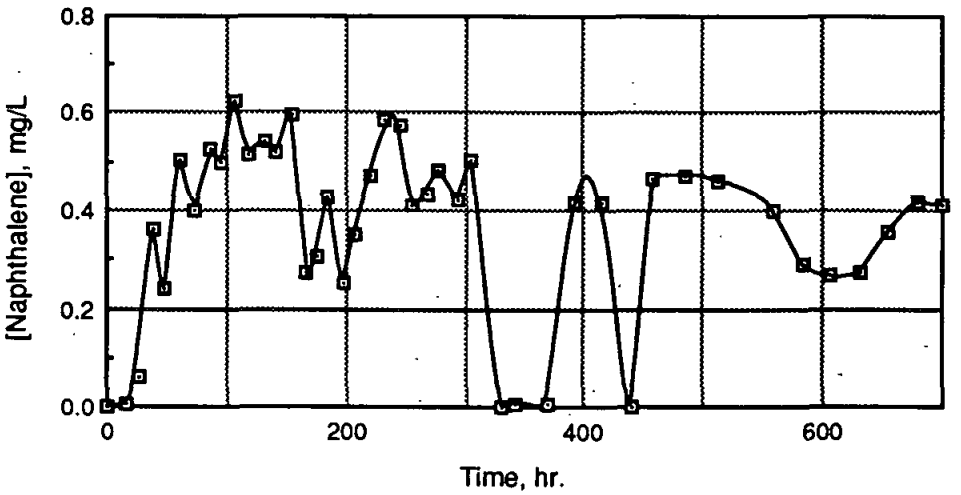


Figure 4.2 Acenaphthylene Concentration in Effluent from Column #1 (0-700 hr)

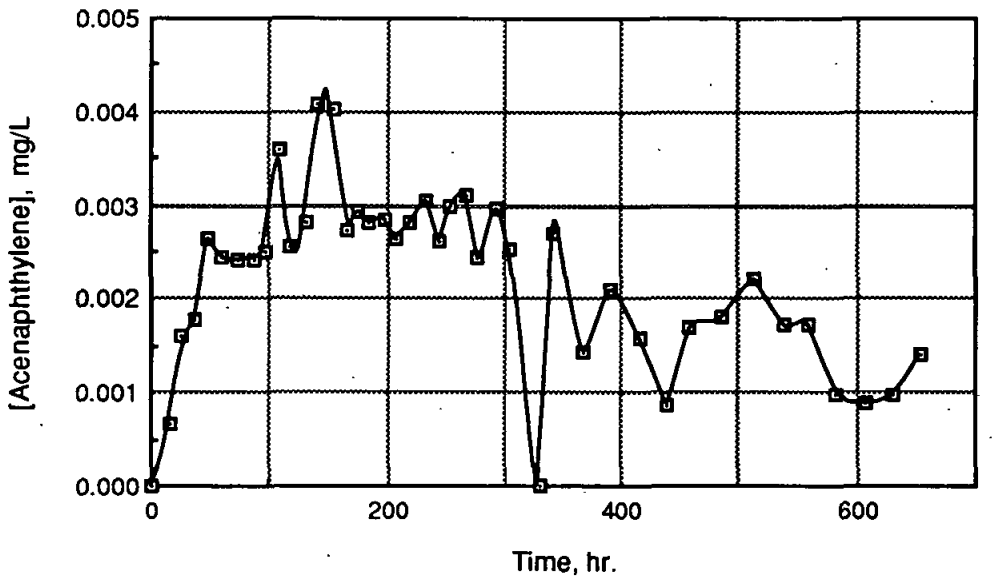


Figure 4.3 Acenaphthene Concentration in Effluent from Column #1 (0-900 hr)

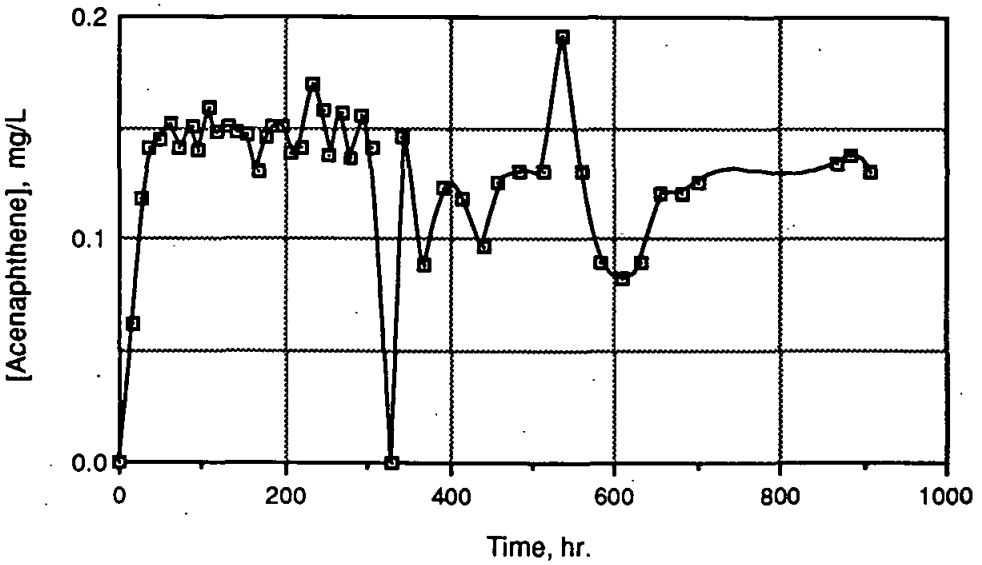


Figure 4.4 Fluorene Concentration in Effluent from Column #1 (0-700 hr)

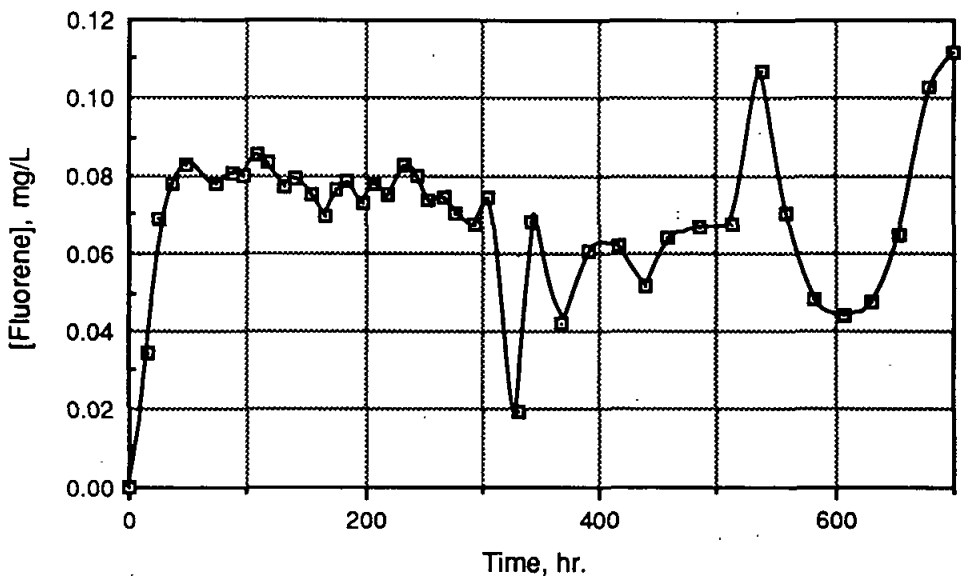


Figure 4.5 Phenanthrene Concentration in Effluent from Column #1 (0-700 hr)

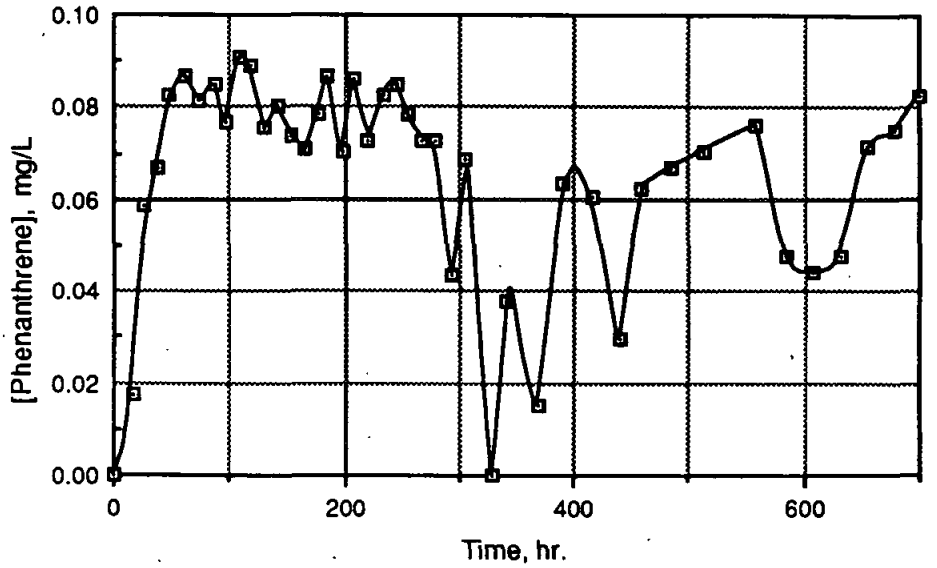


Figure 4.6 Anthracene Concentration in Effluent from Column #1 (0-700 hr)

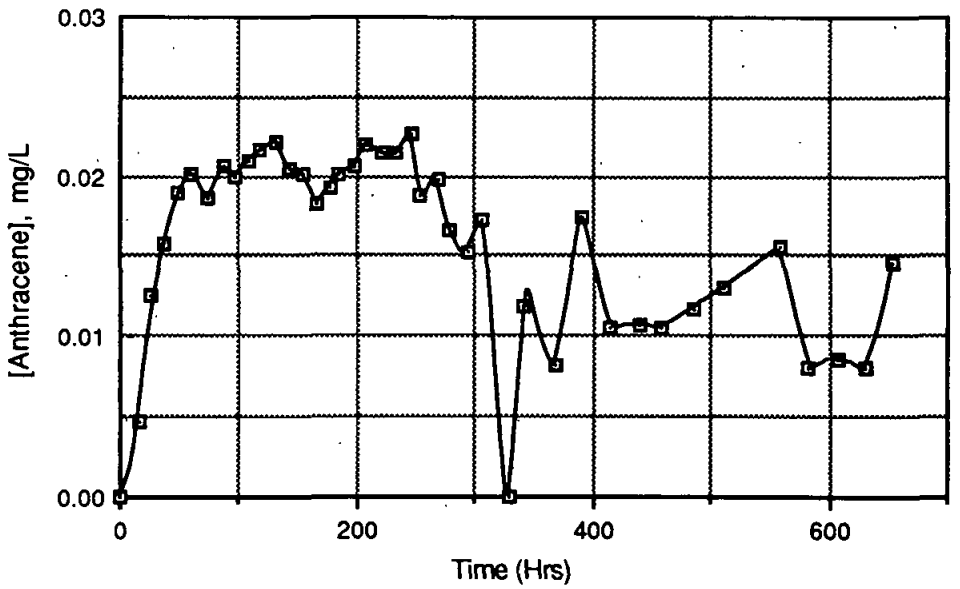


Figure 4.7 Fluoranthene Concentration in Effluent from Column #1 (0-700 hr)

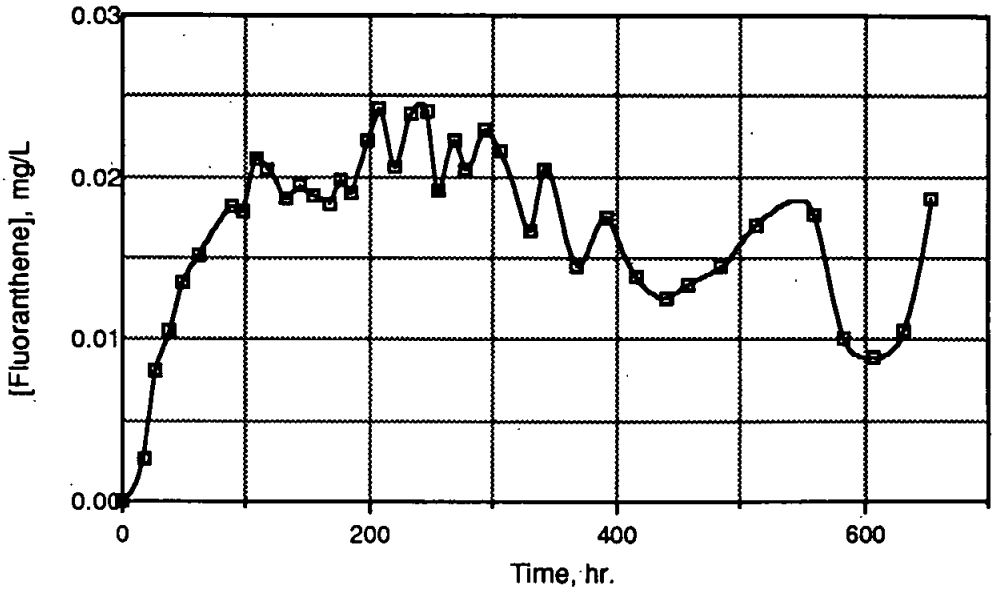


Figure 4.8 Pyrene Concentration in Effluent from Column #1 (0-700 hr)

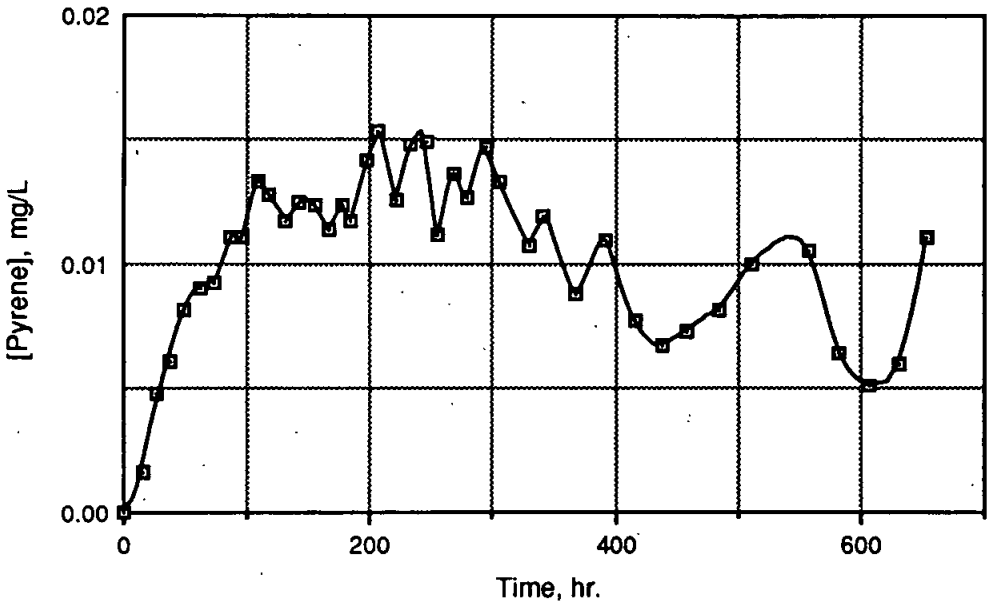


Figure 4.9 Naphthalene Concentration in Effluent from Column #1 (850-2700 hr)

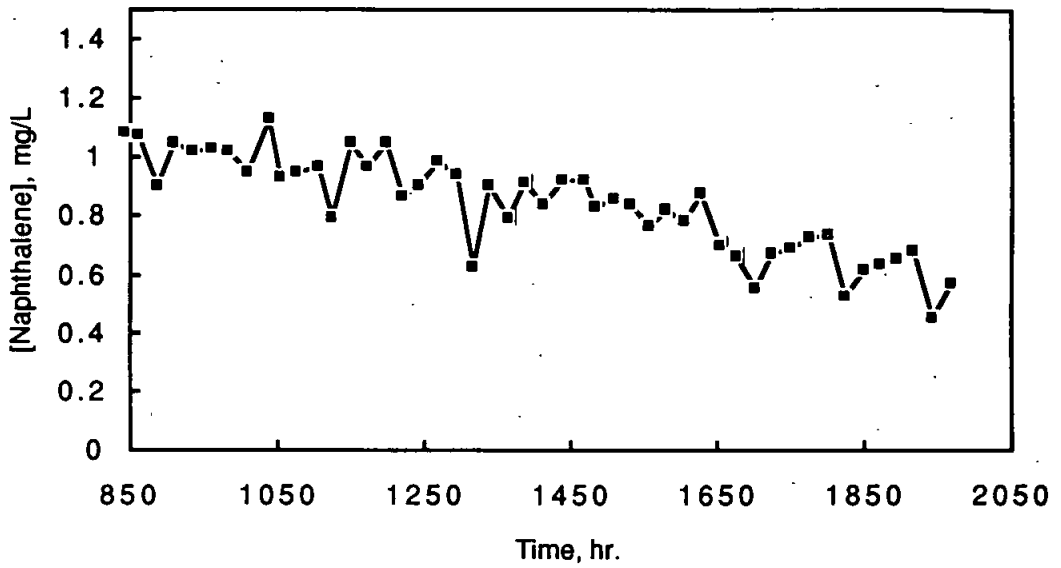


Figure 4.10 Acenaphthene Concentration in Effluent from Column #1 (850-2700 hr)

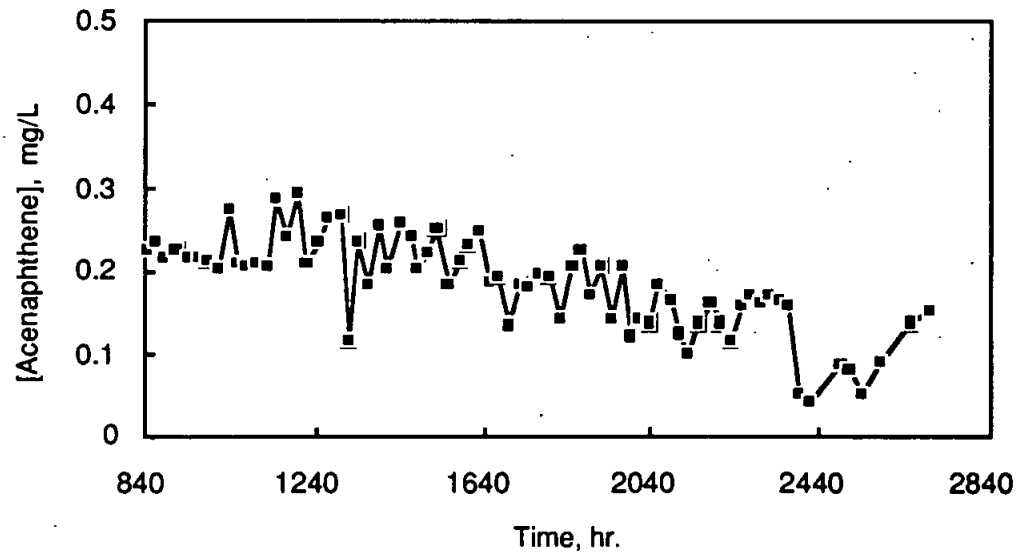


Figure 4.11 Fluorene Concentration in Effluent from Column #1 (850-2700 hr)

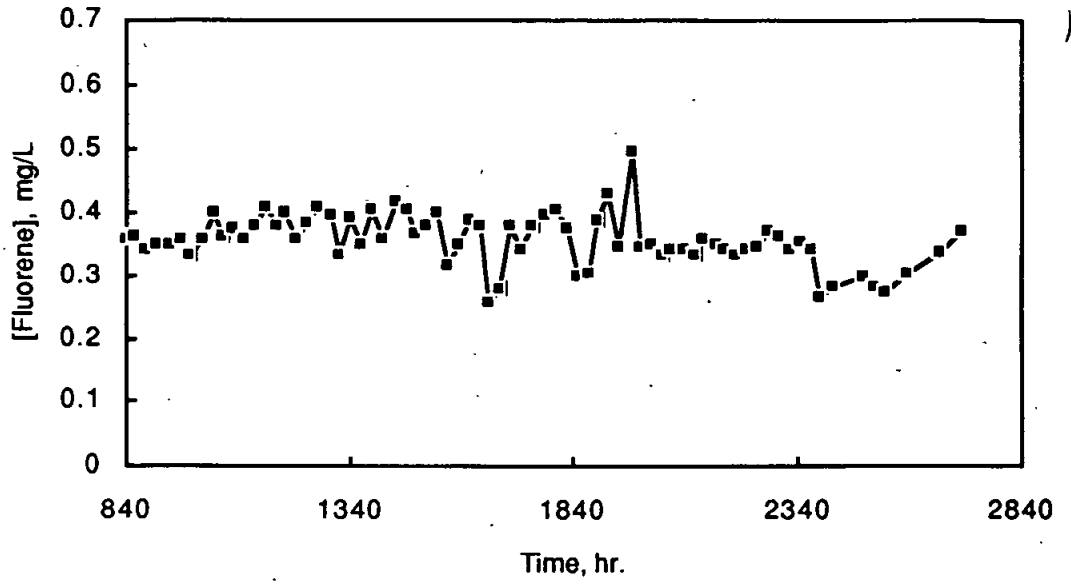


Figure 4.12 Phenanthrene Concentration in Effluent from Column #1 (850-2700 hr)

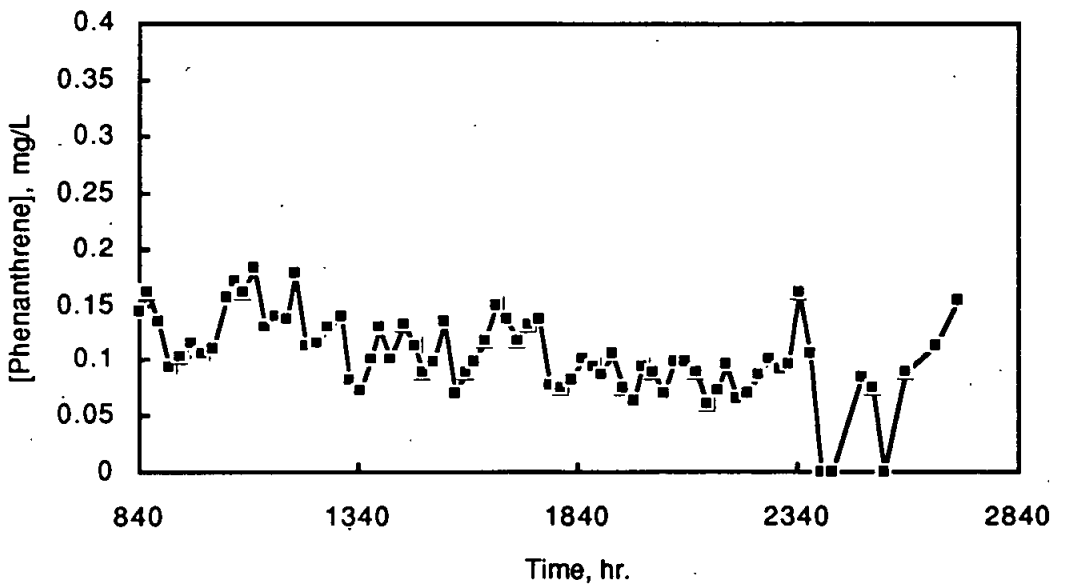


Figure 4.13 Concentration Profile of Phenanthrene at Various Depths of Column #1

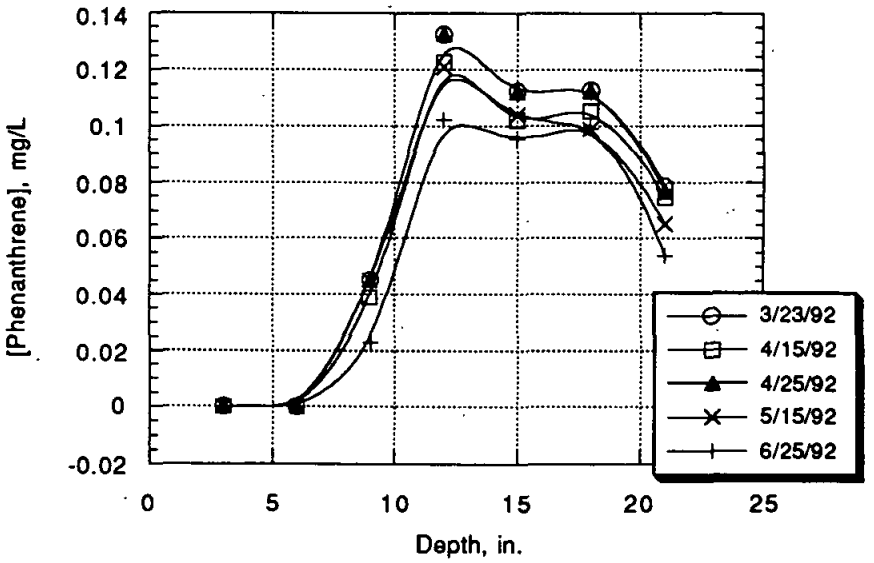


Figure 4.14 Concentration Profile of Naphthalene at Various Depths of Column #1